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EXAMINER

GOODROW, JOHN L

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1756

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Please find below and/or attached an Office communication concerning this application or proceeding.

Response to Rule 312 Communication	Application No.	Applicant(s)	
	10/806,013	YAMANE ET AL.	
	Examiner	Art Unit	
	John L. Goodrow	1756	

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1. ☐ The amendment filed on 19 October 2006 under 37 CFR 1.312 has been considered, and has been:

a) ☒ entered.

b) ☐ entered as directed to matters of form not affecting the scope of the invention.

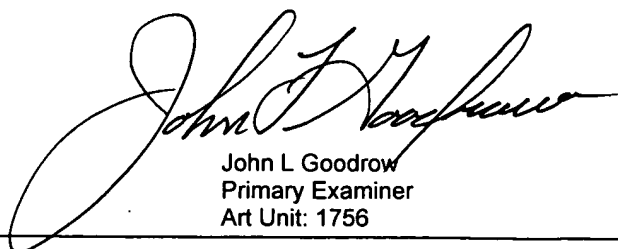
c) ☐ disapproved because the amendment was filed after the payment of the issue fee.

Any amendment filed after the date the issue fee is paid must be accompanied by a petition under 37 CFR 1.313(c)(1) and the required fee to withdraw the application from issue.

d) ☐ disapproved. See explanation below.

e) ☐ entered in part. See explanation below.

A copy of an English translation of JP-2002-148848 is attached


 John L. Goodrow
 Primary Examiner
 Art Unit: 1756

PATENT ABSTRACTS OF JAPAN

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(71)Applicant : KONICA CORP

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OMURA TAKESHI
YAMANOUCHI TAKAO**(54) ELECTROSTATIC CHARGE IMAGE DEVELOPING TONER, ELECTROSTATIC CHARGE IMAGE DEVELOPER, METHOD FOR DEVELOPING, METHOD AND DEVICE FOR IMAGE FORMING**

(57)Abstract:

PROBLEM TO BE SOLVED: To provide electrostatic charge image developing toner, electrostatic charge image developer, a developing method, an image forming method and an image forming device which are not affected by the temperature and humidity of use environment and with/by which a defective image such as the deterioration of image density and the occurrence of fogging is not caused in spite of use over a long term.

SOLUTION: In the electrostatic charge image developing toner incorporating a resin, a colorant and an additive, at least one kind of the additive is titanium oxide particles including silica.

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Notes:

1. Untranslatable words are replaced with asterisks (****).
2. Texts in the figures are not translated and shown as it is.

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Dictionary: Last updated 09/29/2006 / Priority: 1. Chemistry / 2. Natural sciences

FULL CONTENTS

[Claim(s)]

[Claim 1] Toner for static charge image development characterized by at least one of said the external additives being a silica intension titanium oxide particle in the toner for static charge image development containing resin, a colorant, and an external additive.

[Claim 2] Toner for static charge image development according to claim 1 characterized by silica of said silica intension titanium oxide particle and the percentage of titanium oxide being titanium oxide 5 - 40 mass parts to a silica 100 mass part.

[Claim 3] Toner for static charge image development according to claim 1 or 2 which the surface treatment of said silica intension titanium oxide particle is carried out by a hydrophobing agent, and is characterized by the concentration of a titanium atom being 0.02 - 5atm% by measurement by ESCA.

[Claim 4] Toner for static charge image development given in any 1 clause of Claim 1 -3 characterized by for the volume resistivity of said silica intension titanium oxide particle being 10¹¹-10¹⁴-ohmcm, and a moisture content being 0.3 to 1.3 mass % under the 30-degree-C80%RH environment.

[Claim 5] Toner for static charge image development given in any 1 clause of Claim 1 -4 to which primary mean particle diameter of said silica intension titanium oxide particle is characterized by 11-120nm and a BET value being [40-200g/m² and the degree of hydrophobing] 40 to 80%.

[Claim 6] Toner for static charge image development given in any 1 clause of Claim 1 -5 characterized by a number coefficient of variation [in / in the coefficient of variation of the shape factor of toner grains / number particle size distribution] being 27% or less at 16% or less.

[Claim 7] Toner for static charge image development given in any 1 clause of Claim 1 -6 characterized by the percentage of the toner grains which have the shape factor of toner

grains in the range of 1.0-1.6 being several 65 percent or more.

[Claim 8] Toner for static charge image development given in any 1 clause of Claim 1 -6 characterized by the percentage of the toner grains which have a shape factor in the range of 1.2-1.6 being several 65 percent or more.

[Claim 9] Toner for static charge image development according to claim 8 characterized by the coefficient of variation of the shape factor of toner grains being 16% or less.

[Claim 10] Toner for static charge image development given in any 1 clause of Claim 1 -9 characterized by the percentage of toner grains without an angle being several 50 percent or more.

[Claim 11] Toner for static charge image development according to claim 10 characterized by the number coefficient of variation in the number particle size distribution of said toner grain being 27% or less.

[Claim 12] Toner for static charge image development given in any 1 clause of Claim 1 -11 characterized by the number mean particle diameter of toner grains being 3-8 micrometers.

[Claim 13] When setting the grain size of toner grains to D (micrometer), the natural logarithm $\ln D$ for a horizontal axis The relative frequency of the toner grains contained in the modal class in the histogram which shows the particle size distribution of the number basis which divided this horizontal axis into two or more classes at 0.23 intervals (m_1), Claim 1 characterized by the sum (M) with the relative frequency (m_2) of the toner grains contained in class with high frequency after said modal class being 70% or more - toner for static charge image development given in 12 any 1 clauses.

[Claim 14] Toner for static charge image development given in any 1 clause of Claim 1 -13 characterized by being obtained by making a polymerization nature monomer polymerize in a basin system medium.

[Claim 15] Toner for static charge image development given in any 1 clause of Claim 1 -14 characterized by being obtained by making a resin particle meet in a basin system medium.

[Claim 16] Toner for static charge image development given in any 1 clause of Claim 1 -5 characterized by for resin being the composite resin grains obtained by the multistage polymerizing method, being toner obtained by carrying out curing salting/weld of these composite resin grains and the color particle, and the release agent containing to fields other than the outermost layer of this composite resin grain.

[Claim 17] The static charge image developer to which this toner is characterized by being toner for static charge image development given in any 1 clause of Claim 1 -16 in the static charge image developer containing a magnetic carrier with a volume average particle diameter of 12-100 micrometers and toner.

[Claim 18] The development method characterized by using a static charge image developer according to claim 17 for this developer in the development method of contacting the

developer layer and the electrostatic latent image support which were formed on developer support, and developing an electrostatic latent image.

[Claim 19] In the development method that either developer support or electrostatic latent image support has elasticity, and it controls the amount of conveyances of the developer on developer support by a press regulation member The development method characterized by the toner which the thrust of said press regulation member is in the range of 10 N/m - 100 N/m, and uses for a developer being toner for static charge image development given in any 1 clause of Claim 1 -16.

[Claim 20] The developer containing toner and a carrier is conveyed to a development field by developer support in the amount of conveyances of 0.3 - 10.0 mg/cm². The development method characterized by this toner being toner for static charge image development given in any 1 clause of Claim 1 -16 in the development method which only toner is made to fly and is developed on the electrostatic latent image organizer in which the electrostatic latent image which counters developer support was formed.

[Claim 21] The image formation method characterized by using the development method of a description for any 1 clause of Claim 18 -20.

[Claim 22] The electrostatic latent image formed on the electrostatic latent image organizer is developed by the developer containing toner. In the image formation method of performing the toner recycling which conveys the toner which cleaned the toner which remained on the electrostatic latent image organizer, and was collected in this cleaning after transferring the toner image on this electrostatic latent image organizer to transcription material to a development counter The image formation method characterized by this toner being toner for static charge image development given in any 1 clause of Claim 1 -16.

[Claim 23] Image formation equipment characterized by using the image formation method according to claim 21 or 22.

[Detailed Description of the Invention]

[0001]

[Field of the Invention] The toner for static charge image development with which this invention is used for electrophotography (it is also only henceforth called toner), It is especially related with toner, the developer for static charge image development (it is also only henceforth called a developer), the development method, the image formation method, and image formation equipment using the silicon oxide (silica) which is a kind of inorganic particles as an external additive.

[0002]

[Description of the Prior Art] Generally the dry developing method using the magnetic brush etc. as the image formation method of the electrophotography method using the toner for static charge image development is conventionally used from the viewpoint of simplicity. In the above-mentioned development method -- an electrostatic latent image organizer (henceforth -- an electrophotography photo conductor --) Or an electrostatic latent image is only formed in the surface called photo conductor, toner development of this electrostatic latent image is carried out using a magnetic brush etc., the obtained toner image is transferred on transcription material using means, such as electrostatic transcription, finally the means of a hot calender roll etc. is used, toner is fixed on transcription material, and it is considered as a permanent picture. The toner which remained without being transferred on an electrostatic latent image organizer is removed by braid cleaning or other means as waste toner.

[0003] By this method, to diameter[of a granule]-ize the grain size of toner is desired from a high-definition viewpoint. In this diameter[of a granule]-ized toner, since adsorption of moisture etc. increases and change of electrostatic property etc. increases what is called according to the change of a service condition when surface area increases, it is difficult for it to be stabilized and to form a picture.

[0004] Moreover, electrostatic property and fluid grant are made by adding external additives, such as inorganic particles, to coloring grains to the toner for electrophotography. As what reduces environment dependency, hydrophobic titanium oxide is already variously indicated as this inorganic particle, for example in each gazette, such as a JP,59-52255,A number, 62-129861, JP,H5-188633,A, 6-11886, 6-75430, and 7-230179.

[0005] However, when the diameter toner of a granule is used for a long period of time, having continued, the present condition is burial of the inorganic particles to the toner surface etc. occurring, and being stabilized and being unable to maintain the effect of the inorganic particle.

[0006] Moreover, these days, importance came to be attached to the toner recycle which supplies the cleaned waste toner to development again from a viewpoint which loses waste. However, especially in recycling and using waste toner for development, there is a mechanism in which toner is collected / conveyed from a cleaning part to a development part, and burial of inorganic particles has become is easy to be promoted in response to stress, such as this conveyance. Since a surface state will be greatly influenced by inorganic particles and, as for the toner with which the inorganic particle was buried, the moisture content adsorbed by an environmental variation as a result will be changed sharply, Change of electrostatic property is expanded because a service condition changes, and problems, such as change of image density and a development of KABURI, arise.

[0007] As mentioned above, toner which can maintain the quality of image continued and stabilized at the long period of time without receiving an environmental change is desired.

[0008]

[Problem to be solved by the invention] The purpose of this invention is not influenced by the temperature and humidity of a service condition, but there is in offering the toner for static charge image development, the static charge image developer, the development method, the image formation method, and image formation equipment which do not produce picture defects, such as a fall of image density, and a development of KABURI, even if it uses it for a long period of time, continuing.

[0009]

[Means for solving problem] The above-mentioned purpose is attained by the following composition.

[0010] 1. Toner for static charge image development characterized by at least one of said the external additives being silica intension titanium oxide particle in toner for static charge image development containing resin, colorant, and external additive.

[0011] 2. Toner for static charge image development given in said 1 characterized by silica of said silica intension titanium oxide particle and percentage of titanium oxide being titanium oxide 5 - 40 mass parts to silica 100 mass part.

[0012] 3. Said 1 which surface treatment of said silica intension titanium oxide particle is carried out by hydrophobing agent, and is characterized by concentration of titanium atom being 0.02 - 5atm% by measurement by ESCA, or toner for static charge image development given in 2.

[0013] Toner for static charge image development given in said any 1 clause of 1-3 characterized by for the volume resistivity of said silica intension titanium oxide particle being 10¹¹-10¹⁴-ohmcm, and a moisture content being 0.3 to 1.3 mass % under the 4.30-degree-C80%RH environment.

[0014] 5. Toner for static charge image development given in said any 1 clause of 1-4 to which primary mean particle diameter of said silica intension titanium oxide particle is characterized by 11-120nm and BET value being [40-200g/m² and the degree of hydrophobing] 40 to 80%.

[0015] 6. Toner for static charge image development given in said any 1 clause of 1-5 characterized by number coefficient of variation [in / in the coefficient of variation of the shape factor of toner grains / number particle size distribution] being 27% or less at 16% or less.

[0016] 7. Toner for static charge image development given in said any 1 clause of 1-6 characterized by percentage of toner grains which have shape factor of toner grains in range of 1.0-1.6 being several 65 percent or more.

[0017] 8. Toner for static charge image development given in said any 1 clause of 1-6 characterized by percentage of toner grains which have shape factor in range of 1.2-1.6 being several 65 percent or more.

[0018] 9. Toner for static charge image development given in said 8 characterized by

coefficient of variation of shape factor of toner grains being 16% or less.

[0019] 10. Toner for static charge image development given in said any 1 clause of 1-9 characterized by the percentage of toner grains without an angle being several 50 percent or more.

[0020] 11. Toner for static charge image development given in said 10 characterized by the number coefficient of variation in the number particle size distribution of said toner grain being 27% or less.

[0021] 12. Toner for static charge image development given in said any 1 clause of 1-11 characterized by the number mean particle diameter of toner grains being 3-8 micrometers.

[0022] 13. When Setting Grain Size of Toner Grains to D (Micrometer), Natural Logarithm LnD for Horizontal Axis The relative frequency of the toner grains contained in the modal class in the histogram which shows the particle size distribution of the number basis which divided this horizontal axis into two or more classes at 0.23 intervals (m1), Toner for static charge image development given in said 1 characterized by the sum (M) with the relative frequency (m2) of the toner grains contained in class with high frequency after said modal class being 70% or more - 12 any 1 clauses.

[0023] 14. Toner for static charge image development given in said any 1 clause of 1-13 characterized by being obtained by making a polymerization nature monomer polymerize in a basin system medium.

[0024] 15. Toner for static charge image development given in said any 1 clause of 1-14 characterized by being obtained by making a resin particle meet in a basin system medium.

[0025] 16. Resin is Composite Resin Grains Obtained by the Multistage Polymerizing Method, and it is Toner Obtained by Carrying Out Curing Salting/Weld of These Composite Resin Grains and the Color Particle. Toner for static charge image development given in said any 1 clause of 1-5 characterized by the release agent containing to fields other than the outermost layer of these composite resin grains.

[0026] 17. The static charge image developer to which this toner is characterized by being toner for static charge image development given in said any 1 clause of 1-16 in the static charge image developer containing a magnetic carrier with a volume average particle diameter of 12-100 micrometers and toner.

[0027] 18. The development method characterized by using the static charge image developer of a description for this developer said 17 in the development method of contacting the developer layer and the electrostatic latent image support which were formed on developer support, and developing an electrostatic latent image.

[0028] 19. In the Development Method that Either Developer Support or Electrostatic Latent Image Support Has Elasticity, and it Controls the Amount of Conveyances of Developer on Developer Support by Press Regulation Member The development method characterized by

the toner which the thrust of said press regulation member is in the range of 10 N/m - 100 N/m, and uses for a developer being toner for static charge image development given in said any 1 clause of 1-16.

[0029] 20. Convey Developer Containing Toner and Carrier to Development Field by Developer Support in the Amount of Conveyances of 0.3 - 10.0 Mg/cm². The development method characterized by this toner being toner for static charge image development given in said any 1 clause of 1-16 in the development method which only toner is made to fly and is developed on the electrostatic latent image organizer in which the electrostatic latent image which counters developer support was formed.

[0030] 21. The image formation method characterized by using the development method of a description for said any 1 clause of 18-20.

[0031] 22. Develop Electrostatic Latent Image Formed on Electrostatic Latent Image Organizer by Developer Containing Toner. In the image formation method of performing the toner recycling which conveys the toner which cleaned the toner which remained on the electrostatic latent image organizer, and was collected in this cleaning after transferring the toner image on this electrostatic latent image organizer to transcription material to a development counter The image formation method characterized by this toner being toner for static charge image development given in said any 1 clause of 1-16.

[0032] 23. Image formation equipment characterized by using the image formation method of a description for said 21 or 22.

[0033] This invention is explained in detail hereafter. The toner used for this invention is indicated.

[0034] The toner of this invention is toner which contains a silica intension titanium oxide particle as an external additive (it is also henceforth called an external additive). By applying such toner as the toner or the developer of an electrophotography method, the toner or the developer which has environment dependency small electrification characteristics can be obtained, and a good electrophotography picture can be obtained also in a high-humidity/temperature environment or low-humidity/temperature environment. Moreover, the leak of a charge of such toner can also be small, it can show the electrification characteristics stabilized from the early stages of image formation, and the good picture which change of story tonality, i.e., the concentration rise of a half-tone, crushing of a fine character, etc. do not generate can be obtained.

[0035] The silica intension titanium oxide particle used for this invention is indicated hereafter. The silica intension titanium oxide particle of this invention is a silica intension titanium oxide particle which covered the surface of the silica particle with a titanium oxide particle or titanium oxide membrane.

[0036] By covering the surface of a silica particle with a titanium oxide particle or titanium oxide

membrane, it compares with the usual silica particle, the environment dependency of volume resistivity or a moisture content is small, and when this is applied as an external additive of toner, the toner which makes good image formation possible can be produced.

[0037] Although it is desirable to cover the surface of a silica particle to whole surface homogeneity here as for the covering state of titanium oxide, it is effective also in the state of partial covering.

[0038] The amount of covering of titanium oxide of the silica intension titanium oxide particle of this invention has titanium oxide 5 - 40 desirable mass parts to a silica particle 100 mass part. Especially the desirable range is 10 - 30 mass part. When the amount of covering of titanium oxide carries out continuous use with low-humidity/temperature under in 5 mass parts, there is a problem of an electrification quantity rise and a concentration fall. When more than 40 mass parts, the neglect electrification quantity fall with high-humidity/temperature and change of story tonality are large, and there are problems, like that a filament grows fat and a fine character is crushed.

[0039] As for the primary mean particle diameter of the silica intension titanium oxide particle of this invention, 11-120nm is desirable. A silica intension titanium oxide particle becomes difficult to be buried by having the primary mean particle diameter of this range in a toner parent, i.e., coloring grains, and sufficient flowability for toner can be given, as a result, there is little electrification quantity change of toner and there is little story tonality change of the picture finally obtained.

[0040] In addition, the primary mean particle diameter of a silica intension titanium oxide particle is observed with a transmission electron microscope, and the average of Ferre measured by image analysis is said.

[0041] The manufacture method of the silica particle covered with titanium oxide of this invention is indicated. That is, a silica intension titanium oxide particle is producible with a wet method. As said wet method, a sulfuric acid method and a hydrochloric acid method are mentioned. A sulfuric acid method is explained below as an example of manufacture of the silica intension titanium oxide particle by a wet method.

[0042] The titanium oxide used for this invention dissolves raw materials, such as an ilmenite ore, in sulfuric acid, and removes an impurity by sedimentation etc. While hydrolyzing the obtained solution, after mixing with the seed grain dispersion liquid of the silica particle used as a nucleus, growing up grains by growing up a crystal and drying, high temperature firing can be carried out, it can crack at the end, and the silica intension titanium oxide particle of this invention can be obtained. In addition, it is desirable to perform hydrophobing treatment which carries out a postscript the way things stand since a silica intension titanium oxide particle has high hydrophilic nature. Moreover, it can carry out by adjusting a burning temperature about adjustment of the BET value of this silica intension titanium oxide particle etc. Number average

primary particle diameter can be adjusted by the dispersion-liquid concentration of the silica particle in the grain growth step after a hydrolysis etc.

[0043] [the crystal structure] although the crystal structure of the titanium oxide which has covered the surface of the above-mentioned silica intension titanium oxide particle can form the crystal structure of amorphous one, rutile, anatase, a mixed crystal, etc. on condition of the above-mentioned conditions of manufacture, for example, the conditions of a burning temperature, and the grain growth step after a hydrolysis etc. Even if it is which crystal structure, the effect of this invention is demonstrated.

[0044] In order to carry out hydrophobing and to control change of the electrification characteristics by humidity, as for the silica intension titanium oxide particle of this invention, it is desirable to carry out a surface treatment by hydrophobing agents, such as a silane coupling agent. The conditions of desirable hydrophobing are indicated below.

[0045] When these particles are measured by ESCA, as for the silica intension titanium oxide particle of this invention, it is desirable to perform a surface treatment by hydrophobing treatment so that the concentration of a titanium atom may become 0.02 - 5atm%. 0. Less than [0.2atm%], when continuous use is carried out with low-humidity/temperature, there is a problem of an electrification quantity rise and a concentration fall. When larger than 5atm%, the neglect electrification quantity fall with high-humidity/temperature and change of story tonality are large, and there are problems, like that a filament grows fat and a fine character is crushed. Here, with the measuring method of ESCA, the concentration of a titanium atom measures carbon, oxygen, silicon, and a titanium atom, and asks for them from the relative share of a titanium atom in these four atoms.

[0046] The method of processing by the hydrophobing agent which mentions later the silica particle covered with the above-mentioned titanium oxide as the method of hydrophobing treatment can be mentioned. As measured value at the time of measuring by methanol Wetter BIRITI mentioned later as a degree of hydrophobing, 40-80 is desirable.

[0047] As a hydrophobing agent which carries out hydrophobing of the surface of the silica intension titanium oxide particle of this invention For example, what is called coupling agents, silicone oil, etc., such as various titanium coupling agents and a silane coupling agent, are desirable, and hydrophobing agents, such as higher fatty acid metal salt, such as aluminum stearate, zinc stearate, and calcium stearate, also have them. [desirable] The surface treatment which used the silane coupling agent especially is the most desirable.

[0048] The hydrophobing agent and its treatment method for performing hydrophobing treatment of these grains are explained hereafter.

[0049] As a hydrophobing agent for performing the above-mentioned hydrophobing treatment For example, tetrabutyl titanate, tetra-octyl titanate, isopropylisostearoyl titanate, Titanium coupling agents, such as isopropyl TORIDESHIRUBENZEN sulfonyl titanate and bis(dioctyl

PAIRO phosphate) oxy-acetate titanate, are mentioned. As a silane coupling agent, furthermore, gamma-(2-aminoethyl) aminopropyl trimethoxysilane, gamma-(2-aminoethyl) aminopropyl methyl dimethoxysilane, Gamma-methacryloxypropyl trimethoxy silane, a N-beta-(N-vinylbenzyl aminoethyl) gamma-aminopropyl trimethoxysilane hydrochloride, Hexamethyldisilazane, methyl trimethoxysilane, normal butyltrimethoxysilane, Isobutyl trimethoxysilane, hexyl trimethoxysilane, hexyl trimethoxysilane, Octyl trimethoxysilane, decyltrimethoxysilane, dodecyl trimethoxysilane, phenyltrimethoxysilane, o-methylphenyl trimethoxysilane, p-methylphenyl trimethoxysilane, etc. are mentioned. Normal butyltrimethoxysilane and isobutyl trimethoxysilane are especially used preferably from a viewpoint which gives moderate negative triboelectric charging to toner.

[0050] As fatty acid and its metal salt, moreover, undecylic acid, lauric acid, A tridecyl acid, a dodecyl acid, myristic acid, palmitic acid, pentadecyl acid, Long chain fatty acid, such as stearin acid, a heptadecyl acid, arachin acid, montanic acid, oleic acid, linolic acid, and arachidonic acid, is raised, and a salt with metals, such as zinc, iron, magnesium, an aluminium, calcium, sodium, and lithium, is raised as the metal salt.

[0051] As silicone oil, dimethyl silicone oil, methylphenyl silicone oil, amino modified silicone oil, etc. can be mentioned.

[0052] These compounds are good 5 to 40% addition, and to add 10 to 35% and to cover preferably, to the silica particle covered with the titanium oxide particle, the silica particle, or titanium oxide used as a material, both in quality and in quantity. It can also be used combining such material. Moreover, the surface treatment of the ammonium salt can also be carried out by the polysiloxane which it has as a functional group.

[0053] [the degree of hydrophobing in the silica intension titanium oxide particle of this invention adding 0.1g of silica intension titanium oxide particles to 50ml of distilled water, and agitating this] At 2ml a rate for /, the micro inner tube pump was used for these dispersion liquid, methanol was added to them, and it asked from methanol concentration when a silica intension titanium oxide particle carries out a sedimentation start and carries out humidity completely (when the silica intension titanium oxide particle of the water surface distributes underwater).

[0054] When quantity of methanol required in order to carry out humidity of the silica intension titanium oxide particle completely is set to a (ml), the degree of hydrophobing is computed by the following formula.

[0055]

Degree $= (a / (a + 50)) \times 100$ (%)

In addition, the desirable mode of the silica intension titanium oxide particle of this invention is indicated.

[0056] As for the silica intension titanium oxide particle of this invention, it is desirable that

1011-1014ohms of volume resistivity cm and the moisture content under the conditions of 30-degree-C80%RH (RH: relative humidity) are 0.3 to 1.3 mass %. Under in 1011-ohmcm, a neglect electrification quantity fall and change of story tonality are large, and there are problems, like that a filament grows fat and a fine character is crushed. On the other hand, when larger than 1014-ohmcm and continuous use is carried out, there is a problem of an electrification quantity rise and a concentration fall.

[0057] Measurement of the above-mentioned volume resistivity measured ***** of the silica intension titanium oxide particle using equipment as shown in drawing 1 , and made this value volume resistivity. In this figure, the pipe of insulation [51 / 52 / a measurement particle layer (sample layer) and], the weight of the product [53] made from brass, the bottom plate of the product [54] made from brass, and 55 are ohm-meters.

[0058] It asked for ***** by the following formula from the reading value R of an ohm-meter (omega), the cross-section area S of a sample layer (cm²), and sample layer thickness t (cm). In addition, in this measurement, 500g/cm² of load is applied to a sample layer.

[0059] ***** (omegacm) = measurement of the $R \times S / t$ above-mentioned moisture content is performed by Karl Fischer technique measuring apparatus "AQS-724" (made by Hiranuma Sangyo Co., Ltd.), and especially in that case, cautions are required and it is good for a sampling to carry out as follows.

[0060] The silica intension titanium oxide particle of this invention is extracted as a sample into a bottle with a screw with packing for exclusive use under each environmental atmosphere, i.e., the environmental condition of 30 degrees C / 80RH%, and a lid is shut in the atmosphere. The silica particle covered with the titanium oxide sampled if a lid was not shut in the atmosphere is influenced by atmosphere, and an exact moisture content is not obtained (since in an instant comes the moisture content of the atmosphere). In measurement of the moisture content of the silica particle covered with titanium oxide of this invention, the influence of weak physical adsorption of bonding strength is also important, and careful cautions are required for measurement. It measures by extracting the air under the atmosphere as an object for comparison.

[0061] On the occasion of that measurement, measurement of the above-mentioned volume resistivity and a moisture content neglects a sample under the environmental condition of 30 degrees C / 80RH% for at least 1 hour or more, and adjusts the moisture content of a sample etc. to a state of equilibrium under this environmental condition.

[0062] Moreover, as for the silica intension titanium oxide particle of this invention, it is desirable that 11-120nm and a BET value (BET surface area) are [40-200g/m² and the degree of hydrophobing of primary mean particle diameter] 40 to 80%.

[0063] While giving moderate flowability to toner when primary mean particle diameter is 11-120nm as described above A silica intension titanium oxide particle becomes difficult to be

buried in a toner parent, i.e., coloring grains, as a result, there is little electrification quantity change of toner, and there is little story tonality change of the picture obtained as a result. [0064] Moreover, when the BET value of a silica intension titanium oxide particle is 40-200g/m² and the degree of hydrophobing is 40 to 80%, the toner using this external additive has little environment dependency of electrification, and filming to a photo conductor does not generate it. With less than 40% of the degree of hydrophobing, the fall of the neglect electrification quantity of toner especially becomes large easily, change of the story tonality of the picture obtained is large, a filament grows fat, and there are problems, like a fine character is crushed. On the other hand, when larger than 80% of the degree of hydrophobing, an electrification quantity rise of the toner in damp environment is large, and there is a problem of being easy to generate the fall of image density.

[0065] Measurement of the above-mentioned BET specific surface area used "GEMINI2375" (made by Shimadzu Corp.), and measured it by the one-point method of the nitrogen adsorption process.

[0066] Although the toner of this invention mixes coloring grains and a silica intension titanium oxide particle at least and it is constituted, the blending ratio of coal of a silica intension titanium oxide particle has a desirable 0.01 - 5.0 mass part to a coloring grain 100 mass part, and its 0.01 - 2.0 mass part is especially desirable.

[0067] If there is little loadings of a silica intension titanium oxide particle, a bad influence will occur in development, for example, it is easy to generate the problem of image density falling. On the other hand, adhesion of toner occurs that it is excessive on a developing sleeve or a photo conductor, and a picture defect occurs.

[0068] Next, the toner composition of those other than the above-mentioned external additive used for this invention is indicated. The toner of this invention mixes an external additive to the coloring grains which contain resin and a colorant at least, and is produced. Although the coloring grains before mixing this external additive are divided roughly and have resin, the grinding method by kneading of a colorant, and grinding, and the polymerizing method that forms coloring grains chemically, the toner of this invention can demonstrate a more prominent effect by using the toner produced by the polymerizing method. That is, since the toner produced by the polymerizing method can equalize sharply toner form, such as particle size distribution and shape factor distribution, it can make uniform the area density of a silica intension titanium oxide particle, and the effect of using for an external additive shows up notably.

[0069] A description is begun for the composite resin grains preferably used for this invention below from the definition of curing salting / toner made to weld.

[0070] <Definition> The resin which forms the nuclear particle concerned shall mean the resin particle of multi-layer construction in which 1 or two or more enveloping layers which consist of

resin with which molecular weight differs from a presentation are formed so that the "composite resin grains" which constitutes the toner of (1) this invention may cover the surface of the nuclear particle which consists of resin.

[0071] Moreover, the "nuclear particle" from which "the central part (nucleus)" of composite resin grains constitutes composite resin grains is said.

[0072] Moreover, the outermost layer is said between "1 or 2 or more enveloping layers" from which "an outer layer (husks)" of composite resin grains constitutes composite resin grains.

[0073] Moreover, the "interlayer" of composite resin grains shall mean the enveloping layer formed between the central part (nucleus) and an outer layer (husks).

[0074] The molecular weight distribution of composite resin grains is not mono dispersion, and composite resin grains usually have molecular weight inclination from the central part (nucleus) to an outer layer (husks).

(2) [method / for obtaining composite resin grains / "multistage polymerizing method"] in this invention Under existence of the resin particle (n) obtained by carrying out polymerization (the n-th step) of the monomer (n), polymerization (the n+1st step) of the monomer (n+1) is carried out. The method of forming the enveloping layer (n+1) which becomes the surface of the resin particle (n) concerned from the polymer (resin with which dispersion and/or a presentation differ from composition resin of a resin particle (n)) of a monomer (n+1) shall be said.

[0075] When a resin particle (n) is a nuclear particle (n= 1), it becomes the "two-step polymerizing method" here, and when resin particles (n) are composite resin grains (n>=2), it becomes three or more steps of multistage polymerizing methods.

(3) As for "curing salting/weld", say the act which makes that curing salting (condensation of grains) and weld (interface elimination between grains) take place simultaneously, or curing salting and weld cause one by one or simultaneous in this invention.

[0076] In order to make curing salting and weld perform simultaneously, it is necessary to make grains (composite resin grains, color particle) condense under the temperature conditions more than the glass transition temperature (Tg) of the resin which constitutes composite resin grains.

(4) In this invention, a "crushing strength index" is an index which toner grains are crushed and shows easy, and, specifically, say the index called for by the following method.

Toner (sample) 30g and glass bead "GB503M" (Toshiba Ballotini [Co., Ltd.] make particle diameter: 2mm)100g are put into a 2l. polyethylene pot. (Method) After carrying out mixed churning for 60 seconds by the TURBULA mixer, separation removal of the glass bead is carried out by the examination screen of 330 meshes.

[0077] And it sets before and after mixed churning, the number rate (%) of the 2-4-micrometer granule child in all the toner grains is measured, and it computes by the following formula.

[0078] Crushing strength index = (N-N0)/60 (N is number% of pieces of a 2-4-micrometer

granule child after mixed churning among a formula, and NO is number% of pieces of a 2-4-micrometer granule child before mixed churning.)

In addition, "number% of pieces of a granule child" is the value measured using coal tar multiple sizer. Specifically, it is used using coal tar multiple sizer, connecting the interface (product made from a Japanese familial machine) and personal computer which output particle size distribution. Volume distribution of toner of 2 micrometers or more (for example, 2-40 micrometers) was measured and computed, using a 100-micrometer thing as an aperture in said coal tar multiple sizer.

[0079] Several resin with which the composite resin grains obtained by the multistage polymerizing method differ in the presentation and/or molecular weight will exist. The toner obtained curing salting / by making it weld in composite resin grains and a color particle concerned has the very small variation in a presentation, molecular weight, and a surface property among toner grains.

[0080] The crushing strength of the toner with which such toner grains consist of two or more resin composition and molecular weight is high. By applying to the development method of either the developer support of this invention or electrostatic latent image support having elasticity, or having the positioning member which sets the opening distance between both support as a predetermined value between developer support and electrostatic latent image support Weld is prevented and the toner to a developing sleeve top can prevent the development of a picture defect.

[0081] <Composite resin grains> as composite resin grains for obtaining the toner of this invention (1) The central part which has the central part (nucleus) formed from high-molecular weight resin, and the outer layer (husks) formed from low-molecular-weight resin, and is formed in said central part (nucleus) from the composite resin grains which the release agent contains, and (2) high-molecular weight resin (nucleus), It has 1 or two or more interlayers who are formed from the amount resin of intermediate molecules, and the outer layer (husks) formed from low-molecular-weight resin. The composite resin grains which the release agent contains in said interlayer's layer of at least 1, and the central part formed from (3) high-molecular weight resin (nucleus), The central part which has the outer layer (husks) formed from low-molecular-weight resin, and is formed in said central part (nucleus) from the composite resin grains which crystalline polyester contains, and (4) high-molecular weight resin (nucleus), It has 1 or two or more interlayers who are formed from the amount resin of intermediate molecules, and the outer layer (husks) formed from low-molecular-weight resin, and the composite resin grains which crystalline polyester contains in said interlayer's layer of at least 1 can be mentioned.

[0082] Curing salting / by welding, high-molecular weight resin and low-molecular-weight resin can be introduced for the above composite resin grains into the toner of this invention.

[0083] [the "high-molecular weight resin" which constitutes the central part (nucleus) of composite resin grains here] In the molecular weight distribution measured by GPC, it is resin which has a peak or a shoulder in the range of 100,000-1,000,000, and it is desirable that it is what has a peak or a shoulder in the range of 120,000-500,000.

[0084] By introducing this high-molecular weight resin, sufficient internal force of coagulation (offset-proof nature at the time of high temperature) for the toner obtained can be given.

[0085] [moreover, the "low-molecular-weight resin" which constitutes the outer layer (husks) of composite resin grains] In the molecular weight distribution measured by GPC, it is resin which has a peak or a shoulder in the range of 1,000-50,000, and it is desirable that it is what has a peak or a shoulder in the range of 3,000-20,000.

[0086] By introducing this low-molecular-weight resin, the fixability (adhesive strength over a picture base material) excellent in the toner obtained can be given.

[0087] [the "amount resin of intermediate molecules" which constitutes the interlayer of composite resin grains] It is resin which has a peak or a shoulder in the range of 25,000-150,000 in the molecular weight distribution measured by GPC. It is needed for the peak molecular weight of the amount resin of intermediate molecules which constitutes the interlayer of the composite resin grains of 1 to exist between the peak molecular weight of the high-molecular weight resin which constitutes the central part (nucleus) of the composite resin grain concerned, and the peak molecular weight of the low-molecular-weight resin which constitutes the outer layer (husks) of the composite resin grain concerned.

[0088] Thereby, molecular weight inclination is formed between the central part (nucleus) of the composite resin grain concerned, and an outer layer (husks).

[0089] The molecular weight distribution of the resin which constitutes the toner of this invention is the molecular weight of the styrene conversion measured using GPC (gel permeation chromatography).

[0090] As a measuring method of the molecular weight of resin by GPC, 1ml of THF(s) are added to 0.5-5.0mg (specifically 1mg) of test portions, and it agitates using a magnetic stirrer etc. and is made to fully dissolve at a room temperature. Subsequently, after processing with a membrane filter with a pore size of 0.45-0.50 micrometer, it pours in to GPC.

[0091] As a measurement condition of GPC, a column is stabilized at 40 degrees C, THF is passed by the rate of flow of 1ml/m, about 100microl pouring of the sample with a concentration of 1mg/ml is carried out, and it is measured. As for a column, it is desirable to use it combining a commercial polystyrene gell column. For example, Shodex by Showa Denko K.K. GPC The combination of KF-801, 802, 803, and 804,805,806,807, The combination of TSKgelG 1000H by TOSOH CORP., G2000H, G3000H, G4000H, G5000H, G6000H, G7000H, and TSKguardcolumn etc. can be mentioned. Moreover, as a detecting element, it is desirable to use a refractive index detector (IR detecting element) or UV

detecting element. In the determination of molecular weight of a sample, it computes using the calibration curve which measured the molecular weight distribution which a sample has using monodisperse polystyrene standard grains. It is good to use about ten points as polystyrene for calibration curve measurement.

[0092] As a polymerization nature monomer for obtaining the composite resin grains which constitute the toner of this invention, a radical polymerization nature monomer can be used as an indispensable constituent, and a cross linking agent can be used if needed. Moreover, it is desirable to use at least one kind of monomer chosen from the "radical polymerization nature monomer which has an acidic group", and the "radical polymerization nature monomer which has a basic group."

(1) Radical polymerization nature monomer : it is not limited especially as a radical polymerization nature monomer, and a well-known monomer can be conventionally used combining one sort or two sorts or more according to the characteristics demanded.

[0093] As this radical polymerization nature monomer, an aromatic series vinyl monomer, an acrylic ester (meta) system monomer, a vinyl ester system monomer, a vinyl ether system monomer, a mono-olefin system monomer, a diolefin system monomer, a halogenation olefin system monomer, etc. can be mentioned.

[0094] As an aromatic series vinyl monomer, for example Styrene, o-methyl styrene, m-methyl styrene, p-methyl styrene, p-methoxy styrene, p-phenyl styrene, p-chlorostyrene, p-ethyl styrene, p-n-butyl styrene, p-tert-butyl styrene, p-n-hexyl styrene, Styrene monomers, such as p-n-octyl styrene, p-n-nonyl styrene, p-n-decyl styrene, p-n-dodecyl styrene, 2, 4-dimethyl styrene, 3, and 4-dichloro styrene, and the derivative of those are mentioned.

[0095] (Meta) as an acrylic ester system monomer For example, methyl acrylate, ethyl acrylate, butyl acrylate, acrylic acid-2-ethylhexyl, Acrylic acid cyclohexyl, an acrylic acid phenyl, methyl methacrylate, Ethyl methacrylate, methacrylic acid butyl, hexyl methacrylate, Methacrylic acid-2-ethylhexyl, beta-hydroxy ethyl acrylate, gamma-amino acrylic acid propyl, stearyl methacrylate, dimethylaminoethyl methacrylate, diethylaminoethyl methacrylate, etc. are mentioned.

[0096] As a vinyl ester system monomer, vinyl acetate, vinyl propionate, BENZOE acid vinyl, etc. are mentioned, for example.

[0097] As a vinyl ether system monomer, vinyl methyl ether, vinyl ethyl ether, vinyl isobutyl ether, vinyl phenyl ether, etc. are mentioned, for example.

[0098] As a mono-olefin system monomer, ethylene, propylene, isobutylene, 1-butene, 1-pentene, 4-methyl 1-pentene, etc. are mentioned, for example.

[0099] As a diolefin system monomer, butadiene, isoprene, chloroprene, etc. are mentioned, for example.

[0100] As a halogenation olefin system monomer, vinyl chloride, vinylidene chloride, vinyl

bromide, etc. are mentioned, for example.

(2) Cross linking agent : you may add a radical polymerization nature cross linking agent as a cross linking agent for improving the characteristics of toner. As this radical polymerization nature cross linking agent, divinylbenzene, divinyl naphthalene, The compound which has two or more unsaturated bonds, such as divinyl ether, diethylene glycol methacrylate, ethylene glycol dimethacrylate, polyethylene glycol dimethacrylate, and diallyl phthalate, is mentioned. [0101] If the radical polymerization nature cross linking agent occupied to the monomer (monomer mixture) to be used carries out comparatively, it is desirable that it is 0.1 to 10 mass %.

The radical polymerization nature monomer which has an acidic group : (3) as a radical polymerization nature monomer which has an acidic group Acrylic acid, methacrylic acid, boletic acid, maleic acid, itaconic acid, Carboxylic acid group content monomers, such as cinnamic acid, maleic acid monobutyl ester, and maleic acid mono-octyl ester; sulfonic group content monomers, such as styrene sulfonic acid, allyl compound sulfo succinic acid, and allyl compound sulfo succinic acid octyl, are mentioned.

[0102] All or some of radical polymerization nature monomers which has an acidic group may be the structures of alkaline earth metal salt, such as alkali metal salts, such as sodium and potassium, or calcium.

[0103] If the radical polymerization nature monomer which has the acidic group occupied to the monomer (monomer mixture) to be used carries out comparatively, it is 0.1 to 15 mass % that it is 0.1 to 20 mass % desirable still more preferably.

(4) The radical polymerization nature monomer which has a basic group : as a radical polymerization nature monomer which has a basic group, amine system compounds, such as primary amine, secondary amine, tertiary amine, and quarternary ammonium salt, can be mentioned. As an example of this amine system compound, dimethylamino ethyl acrylate, Dimethylaminoethyl methacrylate, diethylaminoethyl acrylate, Diethylamino ethyl methacrylate and these quarternary ammonium salt, 3-dimethylamino phenyl acrylate, a 2-hydroxy 3-metacryloxy propyl trimethylammonium salt, Acrylamide, N-butyl acrylamide, N, and N-dibutyl acrylamide, Piperidyl acrylamide, methacrylamide, N-butyl methacrylamide, N-octadecyl acrylamide; Vinylpyridine, vinyl-pyrrolidone; vinyl N-methyl pyridinium chloride, Vinyl N-ethyl pyridinium chloride, N, and N-diaryl methylammonium chloride, N, and N-diaryl ethylammonium chloride etc. can be mentioned.

[0104] If the radical polymerization nature monomer which has the basic group occupied to the monomer (monomer mixture) to be used carries out comparatively, it is 0.1 to 15 mass % that it is 0.1 to 20 mass % desirable still more preferably.

[0105] [Chain transfer agent] The chain transfer agent generally used for the purpose of adjusting the molecular weight of the resin which constitutes composite resin grains can be

used.

[0106] Especially as a chain transfer agent, it is not limited and For example, octyl mercaptan, Mercaptan, such as dodecyl mercaptan and tert-dodecyl mercaptan, n-octyl 3-mercaptopropionic acid ester, TAPINOREN, carbon tetrabromide, an alpha-methyl styrene dimer, etc. are used.

[0107] [Polymerization initiator] The radical polymerization initiator for obtaining composite resin grains can be suitably used, if it is a water-soluble radical polymerization initiator.

[0108] As an example of a radical polymerization initiator, persulfate (potassium persulfate, ammonium persulfate, etc.), azo system compounds (4 and 4'-azobis 4-cyano valeric acid and its salt, 2, and 2'-azobis (2-amidinopropane) salt etc.), a peroxide compound, etc. are mentioned, for example.

[0109] Furthermore, the above-mentioned radical character polymerization initiator can be combined with a reducing agent if needed, and can be used as a redox system initiator. By using a redox system initiator, polymerization activity can go up, the fall of polymerization temperature can be aimed at, and shortening of polymerization time can be expected further.

[0110] Especially if polymerization temperature is more than the degree of minimum radical student Nariatsu of a polymerization initiator, it will not be limited, but let it be the range of 50-90 degrees C, for example. However, it is also possible by using the polymerization initiators of ordinary temperature starts, such as combination, of hydrogen peroxide and a reducing agent (ascorbic acid etc.) to polymerize at a room temperature or the temperature beyond it.

[0111] [Surface active agent In order to polymerize using the above-mentioned radical polymerization nature monomer, it is necessary to perform oil droplet dispersion into a basin system medium using a surface active agent.] In this case, although there is nothing what is limited especially as a surface active agent which can be used, the following ionic surfactant can be mentioned as an example of a suitable thing.

[0112] as an ionic surfactant -- sulfonate (sodium dodecylbenzenesulfonate --) Arylated alkyl polyether sulphone acid sodium, 3, 3-disulfon diphenylurea-4, and 4-diazo ****- amino 8-naphthol 6-sulfonic acid sodium, The alt.carboxybenzene ****- dimethylaniline, 2, 2, 5, and 5-tetramethyl triphenylmethane color 4, 4-diazo ****- beta naphthol 6-sulfonic acid sodium, etc., sulfuric ester salt (sodium dodecyl sulfate and sodium tetradecyl sulfate --) Fatty acid salt (sodium oleate, lauric acid sodium, capric acid sodium, sodium caprylate, caproic acid sodium, stearin acid potassium, oleic acid calcium, etc.), such as pentadecyl sodium sulfate and octyl sodium sulfate, is mentioned.

[0113] Moreover, a nonionic surface active agent can also be used. Specifically Polyethylene oxide, polypropylene oxide, The combination of polypropylene oxide and polyethylene oxide, Ester of ester of polyethylene glycol and a higher fatty acid, alkylphenol polyethylene oxide, a higher fatty acid, ester of polyethylene glycol and a higher fatty acid, and polypropylene oxide,

sorbitan ester, etc. can be mentioned.

[0114] Let it desirable still more preferably for the weighted mean grain size (diameter of a particulate material) of composite resin grains to be in the range of 10-1000nm be the range of 30-300nm.

[0115] This weighted mean grain size is the value measured using the electrophoresis light scattering photometer "ELS-800" (made by an Otsuka electronic company).

[0116] It is desirable still more desirable that it is in the range of 48-74 degrees C, and the glass transition temperature (T_g) of the resinous principle (resin introduced by composite resin grains) which constitutes the toner of this invention is 52-65 degrees C.

[0117] Moreover, as for the softening temperature of the resinous principle concerned, it is desirable that it is in the range of 95-140 degrees C. Here, the glass transition point (T_g) of a resinous principle means the value measured in DSC, and let the intersection of a baseline and inclination of an endothermic peak be a glass transition point. Using a differential scanning calorimeter, after neglecting it for 3 minutes to 100 degrees C at the temperature of rise-in-temperature *Perilla frutescens* (L.) Britton var. *crispa* (Thunb.) Decne., specifically, it cools to a room temperature by the descent temperature of 10 degrees C / min. Subsequently, when this sample is measured by the heating rate of 10 degrees C / min, the intersection of the extension of the baseline below a glass transition point and the tangent which shows the maximum inclination of a before [from the standup portion of a peak / the peak of a peak] is shown as a glass transition point.

[0118] As measuring apparatus, the DSC-7 grade by PerkinElmer, Inc. can be used here.

[0119] Moreover, the softening temperature of a resinous principle means the value measured using the flow tester. A flow tester "CFT-500" (made by Shimadzu) is specifically used. The temperature which flows out of the outflow starting point when carrying out the melting outflow of the 1cm sample three under the path of 1mm of the pore of a dice, 1mm in length, 20kg/cm² of load, and the heating rate of 6 degrees C / conditions of min, and is equivalent to one half of the height of an ending point is shown as softening temperature.

[0120] <Release agent> Curing salting / met type toner grains of the toner of this invention which are obtained by making weld are desirable in the composite resin grains which contain a release agent to fields other than the outermost layer (the central part or interlayer), and a color particle.

[0121] As a release agent which constitutes the toner of this invention, versatility is well-known and what can be distributed underwater can be illustrated. Specifically, amide system waxes, such as natural waxes, such as a denaturation thing of olefin system waxes, such as polypropylene and polyethylene, and these olefin system wax, and carnauba wax, a rice wax, and fatty acid screw amide, etc. can be mentioned.

[0122] What consists of a crystalline ester compound (henceforth "a specific ester compound")

shown with a following general formula (1) as a suitable release agent which constitutes the toner of this invention can be mentioned.

[0123] General-formula (1): $R_1-(OCO-R_2)_n$ (the carbon number in which R_1 and R_2 may have a substituent, respectively shows the hydrocarbon group of 1-40 among a formula, and n is the integer of 1-4.)

<Specific ester compound> In the general formula (1) showing an ester compound, R_1 and R_2 show the hydrocarbon group which may have a substituent, respectively.

[0124] the carbon number of the hydrocarbon group R_1 is set to 1-40 -- desirable -- 1-20 -- it is referred to as 2-5 still more preferably.

[0125] the carbon number of the hydrocarbon group R_2 is set to 1-40 -- desirable -- 16-30 -- it is referred to as 18-26 still more preferably.

[0126] moreover -- n is made into the integer of 1-4 in a general formula (1) -- desirable -- 2-4 - - further -- desirable -- 3-4 -- it is especially referred to as 4 preferably.

[0127] A specific ester compound is suitably compoundable with the dehydration condensation reaction of an alcohol and carboxylic acid.

[0128] As an example of a specific ester compound, illustration compound (1) - (26) is shown below.

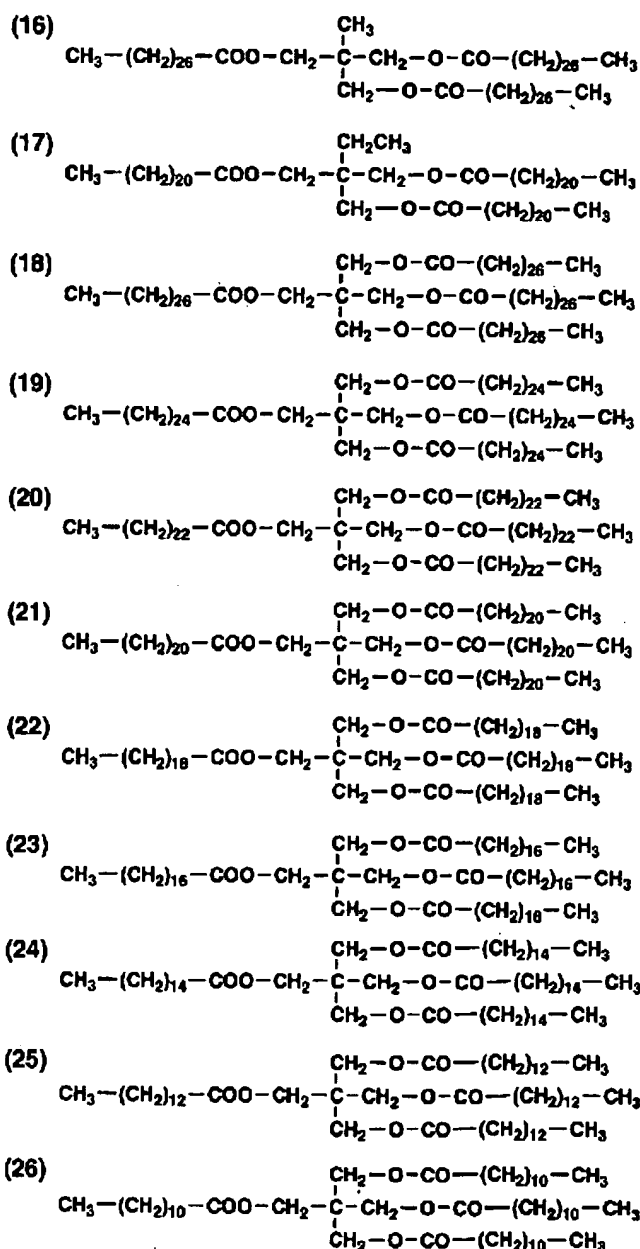
[0129]

[Chemical formula 1]

- (1) $\text{CH}_3-(\text{CH}_2)_{12}-\text{COO}-(\text{CH}_2)_{17}-\text{CH}_3$
- (2) $\text{CH}_3-(\text{CH}_2)_{18}-\text{COO}-(\text{CH}_2)_{17}-\text{CH}_3$
- (3) $\text{CH}_3-(\text{CH}_2)_{20}-\text{COO}-(\text{CH}_2)_{21}-\text{CH}_3$
- (4) $\text{CH}_3-(\text{CH}_2)_{14}-\text{COO}-(\text{CH}_2)_{19}-\text{CH}_3$
- (5) $\text{CH}_3-(\text{CH}_2)_{20}-\text{COO}-(\text{CH}_2)_6-\text{O}-\text{CO}-(\text{CH}_2)_{20}-\text{CH}_3$
- (6)
$$\text{CH}_3-(\text{CH}_2)_{20}-\text{COO}-(\text{CH}_2)_2-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}-\text{CH}_2-\text{O}-\text{CO}-(\text{CH}_2)_{20}-\text{CH}_3$$
- (7)
$$\text{CH}_3-(\text{CH}_2)_{22}-\text{COO}-(\text{CH}_2)_2-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}-\text{CH}_2-\text{O}-\text{CO}-(\text{CH}_2)_{22}-\text{CH}_3$$
- (8)
$$\text{CH}_3-(\text{CH}_2)_{22}-\text{COO}-\text{CH}_2-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}-\text{CH}_2-\text{O}-\text{CO}-(\text{CH}_2)_{22}-\text{CH}_3$$
- (9)
$$\text{CH}_3-(\text{CH}_2)_{26}-\text{COO}-\text{CH}_2-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}-\text{CH}_2-\text{O}-\text{CO}-(\text{CH}_2)_{26}-\text{CH}_3$$
- (10)
$$\begin{array}{c} \text{CH}_2-\text{O}-\text{CO}-(\text{CH}_2)_{28}-\text{CH}_3 \\ | \\ \text{CH}-\text{O}-\text{CO}-(\text{CH}_2)_{26}-\text{CH}_3 \\ | \\ \text{CH}_2-\text{O}-\text{CO}-(\text{CH}_2)_{26}-\text{CH}_3 \end{array}$$
- (11)
$$\begin{array}{c} \text{CH}_2-\text{O}-\text{CO}-(\text{CH}_2)_{22}-\text{CH}_3 \\ | \\ \text{CH}-\text{O}-\text{CO}-(\text{CH}_2)_{22}-\text{CH}_3 \\ | \\ \text{CH}_2-\text{O}-\text{CO}-(\text{CH}_2)_{22}-\text{CH}_3 \end{array}$$
- (12)
$$\begin{array}{c} \text{CH}_2-\text{OH} \\ | \\ \text{CH}-\text{O}-\text{CO}-(\text{CH}_2)_{26}-\text{CH}_3 \\ | \\ \text{CH}_2-\text{O}-\text{CO}-(\text{CH}_2)_{26}-\text{CH}_3 \end{array}$$
- (13)
$$\begin{array}{c} \text{CH}_2-\text{OH} \\ | \\ \text{CH}-\text{O}-\text{CO}-(\text{CH}_2)_{22}-\text{CH}_3 \\ | \\ \text{CH}_2-\text{O}-\text{CO}-(\text{CH}_2)_{22}-\text{CH}_3 \end{array}$$
- (14)
$$\begin{array}{c} \text{CH}_2-\text{OH} \\ | \\ \text{CH}-\text{OH} \\ | \\ \text{CH}_2-\text{O}-\text{CO}-(\text{CH}_2)_{26}-\text{CH}_3 \end{array}$$
- (15)
$$\begin{array}{c} \text{CH}_2-\text{OH} \\ | \\ \text{CH}-\text{OH} \\ | \\ \text{CH}_2-\text{O}-\text{CO}-(\text{CH}_2)_{22}-\text{CH}_3 \end{array}$$

[0130]

[Chemical formula 2]



[0131] <the content ratio of a release agent> -- as the content ratio of the release agent which constitutes the toner of this invention -- usually -- 1 - 30 mass % -- desirable -- further -- desirable -- 2 - 20 mass % -- it is 3 - 15 mass % still more preferably.

[0132] <Content field of the release agent in composite resin grains> In the toner of this invention, the release agent in the composite resin grains which constitute this is contained to fields other than the outermost layer of the composite resin grain concerned (the central part or interlayer).

[0133] Thus, since the release agent to which interparticle adhesive strength is reduced does not contain, the composite resin grains concerned are firmly pasted up on the outermost layer of composite resin grains in curing salting/fusing process, and the high weld grains of crushing strength are formed in it.

[0134] <Crystalline polyester> Curing salting / met type toner grains of the toner of this invention which are obtained by making weld are desirable in the resin particle which contains crystalline polyester to fields other than the outermost layer (the central part or interlayer), and a color particle.

[0135] The crystalline polyester contained in a resin particle here is a compound which gives good fixability (adhesive property over a picture base material) to the toner obtained by making weld the resin particle concerned.

[0136] <Physical properties of crystalline polyester> It shall be desirable still more desirable that it is 50-130 degrees C, and the fusing point of this crystalline polyester shall be 60-120 degrees C.

[0137] According to the crystalline polyester which has a fusing point in the range of 50-130 degrees C, in the toner obtained, it becomes possible to lower the melt viscosity of the whole, and adhesive improvement to paper etc. can be aimed at. And since it is maintained in the range where the elastic modulus by the side of high temperature is desirable even if the crystalline polyester concerned exists, good offset-proof nature is demonstrated. Although the fixability itself improves when the fusing point of crystalline polyester is less than 50 degrees C, a keeping quality falls and a problem is produced in practicality. On the other hand, since melting starting temperature becomes high when a fusing point exceeds 130 degrees C, the contribution to fixable improvement is low and effect exertion of fixable improvement decreases.

[0138] The fusing point of crystalline polyester means the value measured with differential calorimetric analysis equipment (DSC) here. Let temperature which shows the maximum peak of the endothermic peak specifically measured when a rise in temperature (the first rise-in-temperature process) is carried out on condition of 10 degrees C/min from 0 degree C to 200 degrees C be a fusing point. And this fusing point is in agreement with "the endothermic peak (P1) in the first rise-in-temperature process by DSC" mentioned later.

[0139] As concrete measuring apparatus of a fusing point, the DSC-7 grade by PerkinElmer, Inc. can be mentioned.

[0140] It is desirable still more desirable that it is 1,500-15,000, and the number average molecular weight of crystalline polyester is set to 2,000-10,000.

[0141] According to the crystalline polyester which has a number average molecular weight in the range of 1,500-15,000, in the toner obtained, the compatibility in a molten state with binding resin (formless polymer) for demonstrating the melt viscosity fall of the whole improves, and the fixability by the side of low temperature improves more. In the case where this number average molecular weight is less than 1,500, the melt viscosity of crystalline polyester becomes low too much, a compatible state becomes uneven on the contrary easily, and it becomes difficult to improve fixability. On the other hand, when a number average

molecular weight exceeds 15,000, melting of crystalline polyester takes time, and since a compatible state becomes uneven even in this case, the fixable improvement effect will become low.

[0142] The number average molecular weight of crystalline polyester means the value calculated from the molecular weight measured according to the following conditions here. (Conditions)

- Use model : "LC-6A" (made by Shimadzu Corp.)
- Column : "Ultra SUTAIRA gell Plus"
- Analysis temperature : 60 degree C and solvent : M-cresol/chlorobenzene = 3/1 (volume ratio)
- Calibration curve : It is desirable still more desirable that they are 300 or less dPa-s, and melt viscosity (melt viscosity in the fusing point of +20 degrees C) of standard polystyrene calibration curve crystallinity polyester is made into 250 or less dPa-s.

[0143] According to crystalline polyester whose melt viscosity is 300 or less dPa-s, in the toner obtained, it becomes possible to lower the melt viscosity of the whole including binding resin, and fixability improves. Since the whole melt viscosity becomes high when this melt viscosity exceeds 300 dPa-s, the fixable improvement effect will become low.

[0144] The melt viscosity (melt viscosity in the fusing point of +20 degrees C) of crystalline polyester means the value measured with the cone plate viscometer here.

[0145] The peak molecular weight in GPC of crystalline polyester is set to 6,000-50,000.

[0146] As for crystalline polyester, it is desirable that 50-130 degrees C of endothermic peaks (P1) in the first rise-in-temperature process by DSC exist in 60-120 degrees C especially.

[0147] Moreover, as for crystalline polyester, it is desirable that 30-110 degrees C of exothermic peaks (P2) in the first cooling process by DSC exist in 40-120 degrees C especially.

[0148] As for an endothermic peak (P1) and an exothermic peak (P2), the relation of $P1 \geq P2$ is materialized here. Although a difference of temperature (P1-P2) in particular is not restricted, it is desirable that it is 50 degrees C or less.

[0149] By making the crystalline polyester which has the above thermal characteristics contain, the outstanding offset preventive effect (large temperature region which can be established), and the outstanding fixability (high fixing rate) can be demonstrated.

[0150] In order to demonstrate the effect of this invention, it is desirable that binding resin and crystalline polyester exist in the state where it became independent mutually. That is, the operation which dissolves sharply and dissolves binding resin in the state where it fused can work, and crystalline polyester can lower the melt viscosity of the whole toner as a result, and can improve fixability. Moreover, since it becomes possible to suppress decline in the elastic modulus by the side of high temperature by existing independently mutually, offset-proof

nature is not spoiled, either.

[0151] Although fixability improves since the melting temperature is low when an endothermic peak (P1) exists in less than 50 degrees C, offset-proof nature and preservation stability fall.

[0152] Moreover, since the melting temperature is high when an endothermic peak (P1) exists in the range over 130 degrees C, a melting temperature with binding resin becomes high, and fixable improvement cannot be aimed at as a result.

[0153] When the exothermic peak (P2) which shows the state of recrystallization exists in less than 30 degrees C, it cannot recrystallize, unless it cools to a quite low temperature, and crystallinity will exist in toner in the low state, and such a substance cannot be contributed to fixable improvement.

[0154] Moreover, when an exothermic peak (P2) exists in the range over 110 degrees C, the temperature to recrystallize is too high, what is called melting temperature also becomes high, and low-temperature fixability is spoiled.

[0155] An endothermic peak (P1) and an exothermic peak (P2) are measured by differential calorimetric analysis equipment (DSC). As a rise in temperature and cooling conditions, after neglecting it for 1 minute at 0 degree C, a rise in temperature is carried out to 200 degrees C on condition of 10 degrees C/min, and temperature which shows the greatest endothermic peak measured in that case is set to P1. Then, the temperature is lowered on condition of 10 degrees C/min after neglect for 1 minute at 200 degrees C, and temperature which shows the greatest exothermic peak measured in that case is set to P2. As concrete measuring apparatus, the DSC-7 grade by PerkinElmer, Inc. can be mentioned.

[0156] <Constituent of crystalline polyester> The polyester obtained as crystalline polyester by making aliphatic series diol and aliphatic series dicarboxylic acid (acid anhydride and acid chloride being included) react is desirable.

[0157] As diol used in order to obtain crystalline polyester Ethylene glycol, diethylene glycol, triethylene glycol, 1, 2-propylene glycol, 1, 3-propylene glycol, 1, 4-butanediol, 1, 4-butene diol, neopentyl glycol, 1, 5-pentane glycol, 1,6-dihydroxyhexane, 1, 4-cyclohexane diol, 1, 4-cyclohexane dimethanol, Dipropylene glycol, polyethylene glycol, polypropylene glycol, a polytetramethylene glycol, bisphenol A, Bisphenol Z, hydrogenation bisphenol A, etc. can be mentioned.

[0158] As dicarboxylic acid used in order to obtain crystalline polyester Oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, A SUPERIN acid, azelaic acid, sebacic acid, maleic acid, boletic acid, A SHITORAKO acid, itaconic acid, a GURUTAKO acid, n-dodecyl succinic acid, n-dodecenyl succinic acid, iso dodecyl succinic acid, iso dodecenyl succinic acid, n-octyl succinic acid, n-OKUTE nil succinic acid, these acid anhydride, or acid chloride can be mentioned.

[0159] The polyester especially reacted and obtained in 1 and 4-cyclohexane dimethanol and

adipic acid as desirable crystalline polyester, The polyester reacted and obtained in 1,6-dihydroxyhexane and sebacic acid, The polyester reacted and obtained in ethylene glycol and succinic acid, The polyester reacted and obtained in ethylene glycol and sebacic acid, The polyester reacted and obtained in 1 and 4-butanediol and succinic acid can be mentioned, and the polyester reacted and obtained in 1 and 4-cyclohexane dimethanol and adipic acid is [among these] the most desirable.

[0160] <the content ratio of crystalline polyester> -- usually being considered as 2 - 25 mass % as a content ratio of crystalline polyester in the toner of this invention -- desirable -- 5 - 20 mass % -- it is considered as 8 - 15 mass % still more preferably.

[0161] <Content field of crystalline polyester in composite resin grains> In the toner of this invention, crystalline polyester in the composite resin grains which constitute this is contained to fields other than the outermost layer of the composite resin grain concerned (the central part or interlayer).

[0162] Crystalline polyester in composite resin grains is contained to fields other than the outermost layer of the composite resin grain concerned (the central part or interlayer).

[0163] Thus, since the crystalline polyester in which interparticle adhesive strength is reduced does not contain, the composite resin grains concerned are firmly pasted up on the outermost layer of composite resin grains in curing salting/fusing process, and the high weld grains of crushing strength are formed in it.

[0164] <Colorant> The toner of this invention is obtained by carrying out curing salting/weld of the above-mentioned composite resin grains and the color particle.

[0165] As a colorant (color particle with which curing salting/weld with composite resin grains are presented) which constitutes the toner of this invention, various kinds of inorganic pigments, an organic pigment, and a color can be mentioned.

[0166] As an inorganic pigment, a well-known thing can be used conventionally. A concrete inorganic pigment is illustrated below.

[0167] As a black pigment, magnetic powder, such as carbon black, such as furnace black, channel black, acetylene black, thermal black, and lamp black, and also magnetite, and ferrite, is also used, for example.

[0168] These inorganic pigments can carry out [independent or] selection concomitant use of the plurality according to a request. Moreover, the loadings of a pigment is two to 20 mass % to a polymer, and 3 - 15 mass % is chosen preferably.

[0169] When using it as magnetic toner, the above-mentioned magnetite can be added. In this case, it is desirable to do 20-60 mass % addition of into toner from a viewpoint which gives predetermined magnetic properties.

[0170] A thing conventionally well-known also as an organic pigment and a color can be used. A concrete organic pigment and a concrete color are illustrated below.

[0171] As a pigment for magenta or red C. I. pigment red 2, C.I. pigment red 3, C.I. pigment red 5, C.I. pigment red 6, C.I. pigment red 7, C.I. pigment red 15, C.I. pigment red 16, and C.I. pigment red 48: 1, C.I. pigment red 53: 1, C.I. pigment red 57: 1, the C.I. pigment red 122, the C.I. pigment red 123, the C.I. pigment red 139, the C.I. pigment red 144, the C.I. pigment red 149, the C.I. pigment red 166, the C.I. pigment red 177, C. The I. pigment red 178 and C.I. pigment red 222 grade are mentioned.

[0172] As a pigment for Orange or yellow C. I. pigment Orange 31, C.I. pigment Orange 43, the C.I. pigment yellow 12, the C.I. pigment yellow 13, the C.I. pigment yellow 14, the C.I. pigment yellow 15, the C.I. pigment yellow 17, C. The I. pigment yellow 93, the C.I. pigment yellow 94, the C.I. pigment yellow 138, the C.I. pigment yellow 180, the C.I. pigment yellow 185, the C.I. pigment yellow 155, and C.I. pigment yellow 156 grade are mentioned.

[0173] As a pigment for Green or cyanogen, the C.I. pigment blue 15, the C.I. pigment blue 15:2, the C.I. pigment blue 15:3, the C.I. pigment blue 16, the C.I. pigment blue 60, and C.I. pigment Green 7 grade are mentioned.

[0174] moreover, As a color the ** C.I. solvent red 1 -- said -- 49 -- said -- 52 -- said -- 58 -- said -- 63 -- said -- 111 -- said -- 122 and the C.I. solvent yellow 19 -- said -- 44 -- said -- 77 -- said -- 79 -- said -- 81 -- said -- 82 -- said -- 93 -- said -- 98 -- said -- 103 -- said -- 104 -- said -- 112 -- said -- 162 and the C.I. solvent blue 25 -- said -- 36 -- said -- 60 -- said -- 70 -- said -- 93 and these 95 grades can be used and these mixtures can also be used.

[0175] These organic pigments and colors can carry out [independent or] selection concomitant use of the plurality according to a request. Moreover, the loadings of a pigment is two to 20 mass % to a polymer, and 3 - 15 mass % is chosen preferably.

[0176] Surface treatment of the colorant (color particle) which constitutes the toner of this invention may be carried out. As a surface treatment agent, a well-known thing can be used here conventionally, and a silane coupling agent, a titanium coupling agent, an aluminium coupling agent, etc. can specifically be preferably used for it.

[0177] As a silane coupling agent, methyl trimetoxysilane, phenyltrimethoxysilane, Alkoxysilane, such as methylphenyl dimethoxysilane and diphenyldimethoxysilane, Siloxane, such as hexamethyldisiloxane, gamma-chloropropyltrimetoxysilane, Vinyl trichlorosilane, vinyltrimetoxysilane, vinyltriethoxysilane, Gamma-methacryloxypropyl trimethoxy silane, gamma-glycidoxypropyltrimetoxysilane, gamma-mercapto propyltrimethoxysilane, gamma-aminopropyl triethoxysilane, gamma-ureido propyl triethoxysilane, etc. are mentioned.

[0178] TTS marketed as a titanium coupling agent by the trade name called the "PUREN act" by Ajinomoto Co., Inc., for example, 9S, 38S, 41B, 46B, 55, 138S, 238S grade, the commercial item A-1 by Nippon Soda Co., Ltd., B-1, TOT, TST, TAA, TAT, TLA, TOG, TBSTA, A-10, TBT, B-2, B-4, B-7, B-10, TBSTA-400, TTS, TOA-30, TSDMA, TTAB, TTOP, etc. are mentioned.

[0179] As an aluminium coupling agent, "PUREN act AL-M" etc. by Ajinomoto Co., Inc. is

mentioned, for example.

[0180] To a colorant, it is desirable still more desirable that it is 0.01 to 20 mass %, and loadings of these surface treatment agents is made into 0.1 - 5 mass %.

[0181] As a surface treatment method of a color particle, a surface treatment agent can be added in the dispersion liquid of a color particle, and the method to which heat this system and it is made to react can be mentioned.

[0182] After being extracted by filtration and repeating the rinse and filtration treatment by the same solvent, desiccation treatment of the color particle by which surface treatment was carried out is carried out.

[0183] To the toner grains which constitute the toner of this invention, release agents, such as a charge controlling agent, and/or internal agents other than crystalline polyester may contain.

[0184] As a charge controlling agent contained in toner grains, the metal salt of the Nigrosine system color, naphthenic acid, or a higher fatty acid, alkoxyl-ized amine, a quarternary-ammonium-salt compound, an azo system metal complex, salicylic acid metal salt, or its metal complex is mentioned.

[0185] The toner of this invention consists the composite resin grains and color particle containing a release agent of curing salting / met type toner grains which are obtained by making weld.

[0186] One or more domains of a release agent will exist in the submicron field equivalent to the size of composite resin grains, and, as for the toner grains concerned, the release agent was minutely distributed by this toner grain.

[0187] Therefore, while sufficient quantity of a release agent is introduced into the toner of this invention, there is no variation among the toner grains which constitute this in the abundance of a release agent.

[0188] [and the release agent which has the tendency to reduce the adhesive strength between grains, in the composite resin grains with which curing salting/weld is presented] Since it contains to fields other than the outermost layer (the central part or interlayer) and the outermost layer concerned is moreover formed from adhesive good low-molecular-weight resin, composite resin grains paste up firmly and the high weld grains (toner grains) of crushing strength are formed.

[0189] [the crystalline polyester with which the toner of this invention has the tendency to reduce the adhesive strength between grains, in the composite resin grains with which curing salting/weld is presented] Since it contains to fields other than the outermost layer (the central part or interlayer) and the outermost layer concerned is moreover formed from adhesive good low-molecular-weight resin, composite resin grains paste up firmly and the high weld grains (toner grains) of crushing strength are formed.

[0190] Since. [furthermore,] the toner of this invention is met type toner which has the form

which has unevenness in the surface from the manufacture time, welds composite resin grains and a color particle in a basin system medium, and is obtained The form between toner grains and the difference of surface nature become it is very small and uniform [surface nature] as a result easily. For this reason, it is hard to produce a difference in the fixability between toner grains, and fixability can also be kept good.

[0191] <Crushing strength index of toner> The toner of this invention has desirable toner containing resin, a release agent, and a colorant, and it is desirable that the crushing strength index by the above-mentioned definition is 0.1-0.8. The toner of this invention has desirable toner containing resin, crystalline polyester, and a colorant, and its crushing strength index by the above-mentioned definition is [0.1-0.8] desirable.

[0192] If the toner with which a crushing strength index exceeds 0.8 cannot have sufficient shatter resistance but the image formation over a long period of time is presented with such toner, filming, KABURI, carrier SUPENTO, etc. will generate it with the fines produced by crushing.

[0193] On the other hand, the minimum fixing temperature tends to become high and the toner whose crushing strength index is less than 0.1 cannot fully respond to the request of the miniaturization of a copying machine, the reduction in power consumption, etc.

[0194] <Grain size of toner grains> It shall be desirable still more desirable that it is 3-10 micrometers in volume average particle diameter, and the grain size of the toner of this invention shall be 3-8 micrometers. This grain size is controllable by the presentation of the concentration of a flocculant (salting agent), the loadings of an organic solvent, weld time, and a polymer in the manufacture method of the toner explained in full detail behind.

[0195] When volume average particle diameter is 3-10 micrometers, in a fixing process, the large toner particles of adhesion force which it flies [particles], adhere to a heating component and generate offset decrease, and transcription efficiency becomes high, the quality of image of a half-tone improves, and quality of image, such as a filament and a dot, improves.

[0196] The volume average particle diameter of toner can be measured using Coulter counter TA-II, coal tar multiple sizer, SLAD1100 (the Shimadzu Corp. make laser diffraction type grain size measuring apparatus), etc.

[0197] In this invention, it was used using coal tar multiple sizer, having connected the interface (product made from a Japanese familial machine) and personal computer which output particle size distribution. Particle size distribution and mean particle diameter were computed by having measured volume distribution of toner of 2 micrometers or more (for example, 2-40 micrometers), using a 100-micrometer thing as an aperture in said coal tar multiple sizer.

[0198] Furthermore, as toner of this invention, it is desirable that the percentage of a toner grain of 3 micrometers or less is several 20 percent or less, and it is still more desirable that

the percentage of a toner grain of 2 micrometers or less is several 10 percent or less. The quantity of such toner grains (fines toner) can be measured using Otsuka electronic company make and electrophoresis light scattering photometer ELS-800. Thus, in order to adjust particle size distribution, it is desirable to narrow temperature control in curing salting/fusing process. It is carrying out a rise in temperature as quickly as concrete possible, namely, enlarging a heating rate. As this condition, it is still more desirable [the amount of 1-15 degrees-C/] preferably as a heating rate less than 10 minutes less than 30 minutes as time to a rise in temperature.

[0199] When setting the grain size of toner grains to D (micrometer) as toner of this invention, In the histogram which shows the particle size distribution of the number basis which divided this horizontal axis into two or more classes for the natural logarithm $\ln D$ at 0.23 intervals for the horizontal axis It is desirable that the sum (M) of the relative frequency (m1) of the toner grains contained in a modal class and the relative frequency (m2) of the toner grains contained in class with high frequency after said modal class is toner which is 70% or more.

[0200] Since dispersion of the particle size distribution of toner grains becomes narrow when the sum (M) of relative frequency (m1) and relative frequency (m2) is 70% or more, the development of selection development can be certainly controlled by using the toner concerned for an image formation process.

[0201] [the histogram which shows the particle size distribution of the aforementioned number basis] in this invention [the natural logarithm $\ln D$ (D: grain size of each toner grain)] Two or more classes at 0.23 intervals (0-0.23:) 0.23-0.46: 0.46 to 0.69:0.69 to 0.92:0.92 to 1.15:1.15 to 1.38:1.38 to 1.61:1.61 to 1.84:1.84 to 2.07:2.07 to 2.30:2.30 to 2.53:2.53-2.76 -- [the particle size distribution of the number basis divided into ...] It is the shown histogram, and this histogram transmits the grain size data of the sample measured by coal tar multiple sizer according to the following conditions to a computer through an I/O unit, and is created by particle-size-distribution Analysis Program in the computer concerned.

[0202] [Measurement condition]

(1) aperture: -- 100-micrometer(2) sample method-of-preparation: -- electrolyte [ISOTON [] -- add and agitate a proper quantity of surface active agents (neutral detergent) to R-11 (made in coal tar scientific Japan)]50-100ml, and add 10-20mg of test portions to this. It prepares by carrying out the distributed processing of this system for 1 minute with an ultrasonic dispersion machine.

[0203] Moreover, as toner applied to this invention, the toner grains which have a shape factor in the range of 1.2-1.6 are several 65 percent or more, and it is desirable that the coefficient of variation of a shape factor uses the toner which is 16% or less. As for such toner, electrification quantity distribution becomes sharp, and electrostatic property is also stabilized, and it can form good quality of image over a long period of time.

[0204] Moreover, it is desirable that the coefficient of variation of the shape factor of toner is 16% or less, and the number coefficient of variation in the number particle size distribution of toner is 27% or less as toner applied to this invention. By using such toner, it excelled in filament reproducibility and found out that high-definition quality of image could be formed over a long period of time.

[0205] The shape factor of the toner of this invention is shown by the following type, and shows the degree of the roundness of toner grains.

[0206]

shape factor = (an overall diameter/2) (2xpi) / project area -- an overall diameter says the width of the grains from which the interval of the parallel lines serves as the maximum to it, when the projection image to the plane top of toner grains is inserted here by two parallel lines.

Moreover, a project area means the area of the projection image to the plane top of toner grains.

[0207] In this invention, this shape factor took the photograph which expanded toner grains by 2000 times with the scanning electron microscope, and measured it by subsequently analyzing a photographic image using "SCANNING IMAGE ANALYZER" (made by JEOL Co., Ltd.) based on this photograph. Under the present circumstances, the shape factor of this invention is measured in the above-mentioned formula using 100 toner grains.

[0208] Several 65 percent or more has the desirable rate of the toner grains which have a shape factor in the range of 1.0-1.6, several 65 percent or more has the desirable rate of the toner grains which have a shape factor in the range of 1.2-1.6 further, and the toner of this invention is several 70 percent or more most preferably.

[0209] [the toner grains which have this shape factor in the range of 1.0-1.6] by [65 piece] being several percent or more Since the frictional electrification nature in a developer conveyance member etc. becomes more uniform, there is no accumulation of the toner charged too much and it becomes easier to exchange toner than the developer conveyance member surface, it becomes difficult to generate a development ghost's etc. problem. Furthermore, it becomes difficult to crush toner grains, contamination of an electrification grant member decreases, and the electrostatic property of toner is stabilized.

[0210] The coefficient of variation of the shape factor of the toner used for this invention is computed from the following type.

Coefficient-of-variation = $[S/K] \times 100 (\%)$

the inside of [type, and S -- 100 toner -- a particle shape -- the standard deviation of the ** coefficient is shown and K shows the average of a shape factor.]